# PCT

#### WORLD INTELLECTUAL PROPERTY ORGANIZATION International Bureau

# INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPER

WO 98/50007 (11) International Publication Number: (51) International Patent Classification 6: A1 A61K 7/06, 7/50 (43) International Publication Date: 12 November 1998 (12.11.98) (81) Designated States: BR, CN, JP, MX, European patent (AT, PCT/IB98/00651 (21) International Application Number:

(22) International Filing Date: 29 April 1998 (29.04.98)

(30) Priority Data: 5 May 1997 (05.05.97) US 08/851,292

THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH. 45202 (US).

(72) Inventors: GUSKEY, Susan, Marie; 10758 Moss Hill Lane, Montgomery, OH 45249 (US). HALL, Christine; 6072 Dryden Avenue, Cincinnati, OH 45241 (US). ROYCE, Douglas, Allan; 10424 U.S. 50, Aurora, IN 47001 (US). SCHOCH, Kimberly, Ann; 23662 Mt. Meadows Court, Lawrenceburg, IN 47025 (US).

(74) Agents: REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217 (US).

BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published

With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: STYLING SHAMPOO COMPOSITIONS CONTAINING CATIONIC STYLING POLYMERS

#### (57) Abstract

Disclosed are styling shampoo compositions with improved styling performance, and which comprise (a) from about 5 % to about 50 % by weight of a surfactant component selected from the group consisting of a combination of an anionic surfactant and an amphoteric surfactant, and a combination of an anionic surfactant and a zwitterionic surfactant; (b) from about 0,025 % to about 3 % by weight of a cationic deposition polymer having a cationic charge density of from about 0.2 meg/gram to about 2 meg/gram and which is selected from the group consisting of cationic cellulose polymers, cationic guar gum derivatives, and mixtures thereof; (c) from about 0.5 % to about 10 % by weight of an organic cationic hair styling polymer having a cationic charge density of greater than about 2 meq/gram to less than about 4.75 meq/gram; and (d) from about 27 % to about 94.5 % by weight water. Especially effective are those styling shampoo compositions containing a combination of Polyquaternium-16 as the cationic styling polymer, Polyquaternium-10 as a cationic deposition polymer, and a surfactant matrix comprising a combination of ammonium laureth sulfate and cocoamidopropyl betaine.

Control of the Contro

- Park Artistan (1997) - Park Artistan (1997) - 新しては、はありまれが終しました。(1997) - Artistan (1997)

· 图 1、 图 16、 数字类 1600 1 (20) 10 (4)

and the second of the second o

And a second of the second of

The second of th

the transfer of the state of the state of

### FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES '	Spain	•	LS	Lesciho	SE 3	Slovenia
AM	Armenia	FI	Finland		LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	* • •	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon		LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	•	MC	Ménaco 👶 🔭	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia		MD	Republic of Moldova	TG	Togo
BB	Barbados	GE	Ghana		MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea		MK	The former Yugoslav	TM	Turkmenistan
BF	Burkina Faso	GR	Greece		•. •	Republic of Macedonia.	TR	Turkey
BG	Bulgaria	ΗU	Hungary		ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	1733	MN ':>:	Mongolia .	UA -	: Ukraine
BR	Brazil	IL	Israel		MR	Mauritania	UG	Uganda
BY	Belarus	IS	keland	52 B	MW.	Malawi 200 100	US	United States of Americ
CA	Canada	IT .	Italy		MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan		ren i	Miger 1 1 1 1 1 2 2 2 3 3 3 3	Vii	Viet Nam
CG.	Congo	KE.	Kenya		NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	:	NO '	Norway	$\mathbf{z}\mathbf{w}$	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's		NZ	New Zealand		
CM	Cameroon		Republic of Korea		PL	Poland		_
CN	China	KR .	Republic of Korea		PT	Portugal		
CU	Cuba	KZ	Kazakstan		RO	Romania		
CZ	Czech Republic	LC	Saint Lucia		RU	Russian Federation		
DE	Germany	LI	Liechtenstein		SD	Sudan		
DK	Denmark	LK	Sri Lanka		SE	Sweden		
EE	Estonia	LR	Liberia		SG	Singapore		

#### STYLING SHAMPOO COMPOSITIONS CONTAINING CATIONIC STYLING POLYMERS

#### FIELD OF THE INVENTION

The present invention relates to styling shampoo compositions which contain select combinations of cationic deposition polymer and cationic styling polymers to improve the styling performance of the composition, especially when used in select surfactant matrices such as combinations of zwitterionic and anionic surfactants.

### **BACKGROUND OF THE INVENTION**

Many hair shampoo compositions provide acceptable cleaning but provide little or no styling benefits, e.g., body, hold, curl retention, stiffness. To realize such benefits, separate cleaning and styling products are often used.

Recently, hair shampoo compositions have been developed which can provide cleaning and styling performance from a single product. Many of these products contain styling polymers in a compatible shampoo base. To prepare such products, styling polymers can be incorporated into the shampoo base by first dissolving the polymer in a liquid carrier and then adding the polymer/liquid carrier premix to the surfactant phase of the composition. Alternatively, the styling polymer can be dispersed in the surfactant phase of the shampoo composition, and deposited onto the hair to form a thin film on the hair shaft. The polymers provide improved hairstyle benefits such as body, hold, and curl retention. However, some styling polymers, whether deposited onto the hair via a liquid carrier or by dispersion, leave the hair feeling sticky or tacky.

It has now been found that a combination of cationic deposition polymers and select organic cationic styling polymers can be incorporated into shampoo compositions containing select surfactant matrices to improve the styling performance of such compositions. This combination is especially effective in providing both conditioning and styling performance without leaving the hair feeling unduly coated, dirty, sticky, or tacky to the touch. The organic cationic styling polymers defined herein are especially effective in helping provide wet hair conditioning as well as hair styling performance when used in combination with the shampoo matrix defined herein.

In view of the foregoing, it is therefore an object of the present invention to provide a styling shampoo composition with improved styling performance. It is a further object of the present invention to provide improved hairstyle benefits such as hold, body, and curl retention from a styling shampoo composition containing a combination of cationic deposition polymer and organic cationic styling polymer. It is yet another object of the present invention to provide such a composition that also provides some hair conditioning benefits without leaving the hair feeling unduly coated, dirty, sticky or tacky to the touch.

#### SUMMARY OF THE INVENTION

The present invention is directed to styling shampoo c mpositions which comprise from (a) from about 5% to about 50% by weight of a surfactant component selected from the group consisting of a combination of an anionic surfactant and an amphoteric surfactant, and a combination of an anionic surfactant and a zwitterionic surfactant; (b) from about 0.025% to about 3% by weight of a cationic deposition polymer having a cationic charge density of from about 0.2 meq/gram to about 2 meq/gram and which is selected from the group consisting of cationic cellulose polymers; cationic guar gum derivatives, and mixtures thereof; (c) from about 0.5% to about 10% by weight of an organic cationic hair styling polymer having a cationic charge density of greater than about 2 meq/gram to less than about 4.75 meq/gram; and (d) from about 27% to about 94.5% by weight water.

It has been found that select organic cationic styling polymers, preferably Polyquaternium-16, can provide improved styling performance from a shampoo composition when used in combination with a cationic deposition polymer, especially when the cationic polymer combination is also used in combination with select surfactant combinations in the shampoo composition defined herein. The organic cationic styling polymers provide styling benefits such as improved body, hold, and curl retention.

#### DETAILED DESCRIPTION OF THE INVENTION

The styling shampoo compositions of the present invention comprise organic cationic styling polymers which provide the composition with improved styling performance. The styling polymers herein are soluble in water or dispersible in the surfactant phase of the shampoo composition.

The term "water-soluble" as used herein refers to any material that is sufficiently soluble in water to form a substantially clear solution to the naked eye at a concentration of about 0.2% by weight, preferably at about 0.5% by weight, even more preferably at about 1.0% by weight of the material in water at 25°C.

The term "water-insoluble" as used herein refers to any material that is not sufficiently soluble in water to form a substantially clear solution to the naked eye at a concentration of about 0.2% by weight, preferably at about 0.1% by weight of the insoluble material at 25°C.

The styling shampoo compositions of the present invention can comprise, consist of, or consist essentially of the elements and limitations of the invention described herein, as well as any of the additional or optional ingredients, components, or limitations described herein.

All percentages, parts and ratios are by weight of the total composition, unless otherwise specified. All such weights as they pertain to listed ingredients are based on the specific ingredient level and, therefore, do not include carriers or by-products that may be included in commercially available materials, unless otherwise specified.

### Surfactant C mponent

The styling shampoo compositions of the present invention comprise a surfactant component to provide cleaning performance to the composition. The surfactant component in turn comprises a

combination of an anionic surfactant and a zwitterionic surfactant, or a combination of an anionic surfactant and an amphoteric surfactant. Such surfactants should be physically and chemically compatible with the essential components described herein, or should not otherwise unduly impair product stability, aesthetics or performance.

Suitable anionic surfactants for use in the styling shampoo composition herein include those which are known for use in hair care or other personal care cleansing compositions. The concentration of the anionic surfactant in the styling shampoo composition should be sufficient to provide the desired cleaning and lather performance, and generally ranges from about 5% to about 50%, preferably from about 6% to about 30%, more preferably from about 7% to about 25%, even more preferably from about 8% to about 18%, by weight of the composition.

Preferred anionic surfactants suitable for use in the styling shampoo compositions are the alkyl and alkyl ether sulfates. These materials have the respective formulae ROSO<sub>3</sub>M and RO(C<sub>2</sub>H<sub>4</sub>O)<sub>x</sub>SO<sub>3</sub>M, wherein R is alkyl or alkenyl of from about 8 to about 18 carbon atoms, x is an integer having a value of from 1 to 10, and M is a cation such as ammonium, alkanolamines, such as triethanolamine, monovalent metals, such as sodium and potassium, and polyvalent metal cations, such as magnesium, and calcium. Solubility of the surfactant will depend upon the particular anionic surfactants and cations chosen.

Preferably, R has from about 8 to about 18 carbon atoms, more preferably from about 10 to about 16 carbon atoms, even more preferably from about 12 to about 14 carbon atoms, in both the alkyl and alkyl ether sulfates. The alkyl ether sulfates are typically made as condensation products of ethylene oxid and monohydric alcohols having from about 8 to about 24 carbon atoms. The alcohols can be synthetic or they can be derived from fats, e.g., coconut oil, palm kernel oil, tallow. Lauryl alcohol and straight chain alcohols derived from coconut oil or palm kernel oil are preferred. Such alcohols are reacted with between about 0 and about 10, preferably from about 2 to about 5, more preferably about 3, molar proportions of ethylene oxide, and the resulting mixture of molecular species having, for example, an average of 3 moles of ethylene oxide per mole of alcohol, is sulfated and neutralized.

Specific nonlimiting examples of alkyl ether sulfates which may be used in the styling shampoo compositions of the present invention include sodium and ammonium salts of coconut alkyl triethylene glycol ether sulfate, tallow alkyl triethylene glycol ether sulfate, and tallow alkyl hexaoxyethylene sulfate. Highly preferred alkyl ether sulfates are those comprising a mixture of individual compounds, wherein the compounds in the mixture have an average alkyl chain length of from about 10 to about 16 carbon atoms and an average degree of ethoxylation of from about 1 to about 4 moles of ethylene oxide.

Other suitable anionic surfactants are the water-soluble salts of organic, sulfuric acid reaction products conforming to the formula [R<sup>1</sup>-SO<sub>3</sub>-M] where R<sup>1</sup> is a straight or branched chain, saturated, aliphatic hydrocarbon radical having from about 8 to about 24, preferably about 10 to about 18, carbon atoms; and M is a cation described hereinbefore. Nonlimiting examples of such surfactants are the salts of an organic sulfuric acid reaction product of a hydrocarbon of the methane series, including iso-, neo-, and

n-paraffins, having from about 8 to about 24 carbon at ms, preferably about 12 to about 18 carbon atoms and a sulfonating agent, e.g.,  $SO_3$ ,  $H_2SO_4$ , obtained according to known sulfonation methods, including bleaching and hydrolysis. Preferred are alkali metal and ammonium sulfonated  $C_{10}$  to  $C_{18}$  n-paraffins.

Still other suitable anionic surfactants are the reaction products of fatty acids esterified with isethionic acid and neutralized with sodium hydroxide where, for example, the fatty acids are derived from coconut oil or palm kernel oil; sodium or potassium salts of fatty acid amides of methyl tauride in which the fatty acids, for example, are derived from coconut oil or palm kernel oil. Other similar anionic surfactants are described in U.S. Patent 2,486,921; U.S. Patent 2,486,922; and U.S. Patent 2,396,278, which descriptions are incorporated herein by reference.

Other anionic surfactants suitable for use in the styling shampoo compositions are the succinnates, examples of which include disodium N-octadecylsulfosuccinnate; disodium lauryl sulfosuccinate; tetrasodium N-(1,2-dicarboxyethyl)-N-octadecylsulfosuccinnate; diamyl ester of sodium sulfosuccinic acid; dihexyl ester of sodium sulfosuccinic acid; and dioctyl esters of sodium sulfosuccinic acid.

Other suitable anionic surfactants include olefin sulfonates having about 10 to about 24 carbon atoms. In this context, the term "olefin sulfonates" refers to compounds which can be produced by the sulfonation of alpha-olefins by means of uncomplexed sulfur trioxide, followed by neutralization of the acid reaction mixture in conditions such that any sulfones which have been formed in the reaction are hydrolyzed to give the corresponding hydroxy-alkanesulfonates. The sulfur trioxide can be liquid or gaseous, and is usually, but not necessarily, diluted by inert diluents, for example by liquid SO<sub>2</sub>, chlorinated hydrocarbons, etc., when used in the liquid form, or by air, nitrogen, gaseous SO<sub>2</sub>, etc., when used in the gaseous form. The alpha-olefins from which the olefin sulfonates are derived are mono-olefins having from about 10 to about 24 carbon atoms, preferably from about 12 to about 16 carbon atoms. Preferably, they are straight chain olefins. In addition to the true alkene sulfonates and a proportion of hydroxy-alkanesulfonates, the olefin sulfonates can contain minor amounts of other materials, such as alkene disulfonates depending upon the reaction conditions, proportion of reactants, the nature of the starting olefins and impurities in the olefin sulfonate mixture is described in U.S. Patent 3,332,880, which description is incorporated herein by reference.

and the second of the second o

Mornous Company Company (1995)

Another class f anionic surfactants suitable for use in the styling shampoo compositions are the beta-alkyl xy alkane sulfonates. These surfactants conform to the formula

where R<sup>1</sup> is a straight chain alkyl group having from about 6 to about 20 carbon atoms, R<sup>2</sup> is a lower alkyl group having from about 1 to about 3 carbon atoms, preferably 1 carbon atom, and M is a water-soluble cation as described hereinbefore.

Preferred anionic surfactants for use in the styling shampoo compositions include ammonium lauryl sulfate, ammonium laureth sulfate, triethylamine lauryl sulfate, triethylamine laureth sulfate, triethylamine laureth sulfate, monoethanolamine laureth sulfate, monoethanolamine laureth sulfate, include ammonium lauryl sulfate, monoethanolamine laureth sulfate, lauric monoglyceride sodium sulfate, sodium lauryl sulfate, sodium lauryl sulfate, potassium lauryl sulfate, potassium lauryl sulfate, sodium lauryl sarcosine, cocoyl sarcosine, ammonium cocoyl sulfate, ammonium lauroyl sulfate, sodium cocoyl sulfate, sodium lauroyl sulfate, sodium lauroyl sulfate, sodium tridecyl benzene sulfonate, sodium dodecyl benzene sulfonate, and combinations thereof.

Suitable amphoteric or awitterionic surfactants for use in the styling shampoo composition herein include those which are known for use in hair care or other personal care cleansing compositions. Concentrations of such amphoteric surfactants preferably range from about 0.5 % to about 20%, preferably from about 1% to about 10%, by weight of the composition. Nonlimiting examples of suitable zwitterionic or amphoteric surfactants are described in U.S. Patents 5,104,646 (Bolich Jr. et al.), U.S. Patents 5,106,609 (Bolich Jr. et al.), which descriptions are incorporated herein by reference.

Amphoteric surfactants suitable for use in the styling shampoo composition are well known in the art, and these surfactants are most effective when used in combination with the anionic surfactants described herein. Nonlimiting examples of suitable amphoteric surfactants include those surfactants broadly described as derivatives of aliphatic secondary and tertiary amines in which the aliphatic radical can be straight or branched chain and wherein one of the aliphatic substituents contains from about 8 to about 18 carbon atoms and one contains an anionic water solubilizing group such as carboxy, sulfonate, sulfate, phosphate, or phosphonate. Preferred amphoteric surfactants for use in the styling shampoo composition of the present invention include cocoamphoacetate, cocoamphodiacetate, lauroamphoacetate, lauroamphoacetate, and mixtures thereof. Lauroamphoacetate is the most preferred.

Zwitterionic surfactants suitable for use in the styling shampoo composition are well known in the art. Preferably the zwitterionic surfactants are used in combination with the anionic surfactants described herein, and include those surfactants broadly described as derivatives of aliphatic quaternary ammonium, phosphonium, and sulfonium compounds, in which the aliphatic radicals can be straight r

branched chain, and wherein ne of the aliphatic substituents contains from about 8 to about 18 carbon atoms and one contains an anionic group such as carboxy, sulfonate, sulfate, phosphate or phosphonate. Nonlimiting examples of suitable zwitterionic surfactants are the betaines including the high alkyl betaines, such as coco dimethyl carboxymethyl betaine, cocoamidopropyl betaine, cocobetaine, lauryl amidopropyl betaine, oleyl betaine, lauryl dimethyl carboxymethyl betaine, lauryl dimethyl alphacarboxyethyl betaine, cetyl dimethyl carboxymethyl betaine, lauryl bis-(2-hydroxypropyl) carboxymethyl betaine, oleyl dimethyl gamma-carboxypropyl betaine, and lauryl bis-(2-hydroxypropyl)alpha-carboxyethyl betaine. The sulfobetaines may be represented by coco dimethyl sulfopropyl betaine, stearyl dimethyl sulfopropyl betaine, lauryl dimethyl sulfoethyl betaine, lauryl bis-(2-hydroxyethyl) sulfopropyl betaine and the like; amidobetaines and amidosulfobetaines, wherein the RCONH(CH) radical is attached to the nitrogen atom of the betaine are also useful in this invention. Most preferred for use herein is cocoamidopropyl betaine.

Most preferred are surfactant systems comprising a surfactant combination of ammonium laureth sulfate and cocoamidopropyl betaine, especially when used in combination with Polyquaternium-16 as a cationic styling polymer and Polyquaternium-10 as a cationic deposition polymer (both polymers described in detail hereinafter). The surfactant combination of ammonium laureth sulfate and cocoamidopropyl betaine is preferably included in the styling shampoo composition at a weight ratio of ammonium laureth sulfate to cocoamidopropyl betaine of at least about 1.5:1, more preferably at least about 2:1, but preferably not more than about 5:1, more preferably not more than about 10:1.

The styling shampoo compositions of the present invention may further comprise additional surfactants for use in combination with the anionic surfactant component described hereinbefore. Suitable optional surfactants include nonionic surfactants. Any such surfactant known in the art for use in hair or personal care products may be used, provided that the optional additional surfactant is also chemically and physically compatible with the essential components of the styling shampoo composition, or does not otherwise unduly impair product performance, aesthetics or stability. The concentration of the optional additional surfactants in the styling shampoo composition may vary with the cleansing or lather performance desired, the optional surfactant selected, the desired product concentration, the presence of other components in the composition, and other factors well known in the art.

Nonlimiting examples of other anionic, zwitterionic, amphoteric or optional additional surfactants suitable for use in the styling shampoo compositions are described in McCutcheon's, Emulsifiers and Detergents, 1989 Annual, published by M. C. Publishing Co., and U.S. Patent 3,929,678, U.S. Patent 2,658,072; U.S. Patent 2,438,091; U.S. Patent 2,528,378, which descriptions are incorporated herein by reference.

#### Cationic Deposition Polymer

The styling shampoo c mpositions of the present invention comprise an organic cationic deposition polymer as a deposition aid for the styling polymer component described hereinafter.

Concentrations of the cationic deposition polymer preferably range from about 0.025% to about 3%, more preferably from about 0.05% to about 2%, even more preferably from about 0.1% to about 1%, by weight of the composition.

The cationic deposition polymer, excluding the cationic hair styling polymers described hereinafter, for use in the styling shampoo composition of the present invention contains cationic nitrogen-containing moieties such as quaternary ammonium or cationic protonated amino moieties. The cationic protonated amines can be primary, secondary, or tertiary amines (preferably secondary or tertiary), depending upon the particular species and the selected pH of the styling shampoo composition. The average molecular weight of the cationic deposition polymer is between about 10 million and about 5,000, preferably at least about 100,000, more preferably at least about 200,000, but preferably not more than about 2 million, more preferably not more than about 1.5 million. The polymers also have a cationic charge density ranging from about 0.2 meq/gm to about 5 meq/gm, preferably at least about 0.4 meq/gm, more preferably at least about 0.6 meq/gm, but also preferably less than about 3 meq/gm, more preferably less than about 2 meq/gm, at the pH of intended use of the styling shampoo composition, which pH will generally range from about pH 4 to about pH 9, preferably between about pH 5 and about pH 8.

The charge density can be controlled and adjusted in accordance with techniques well known in the art. As used herein the "charge density" of the cationic polymers is defined as the number of cationic sites per polymer gram atomic weight (molecular weight), and can be expressed in terms of meq/gram of cationic charge. In general, adjustment of the proportions of amine or quaternary ammonium moieties in the polymer, as well as pH of the styling shampoo composition in the case of the amines, will affect the charge density.

Any anionic counterions can be use in association with the cationic deposition polymers so long as the polymers remain soluble in water, in the styling shampoo composition, or in a coacervate phase of the styling shampoo composition, and so long as the counterions are physically and chemically compatible with the essential components of the styling shampoo composition or do not otherwise unduly impair product performance, stability or aesthetics. Nonlimiting examples of such counterions include halides (e.g., chlorine, fluorine, bromine, iodine), sulfate and methylsulfate:

The cationic nitrogen-containing moiety of the cationic deposition polymer is generally present as a substituent on all, or more typically on some, of the monomer units thereof. Thus, the cationic deposition polymer for use in the styling shampoo composition includes homopolymers, copolymers, terpolymers, and so forth, of quaternary ammonium or cationic amine-substituted monomer units, optionally in combination with non-cationic monomers referred to herein as spacer monomers. Nonlimiting examples of such polymers are described in the CTFA Cosmétic Ingredient Dictionary, 3rd edition, edited by Estrin, Cr sley, and Haynes, (The Cosmetic, Toiletry, and Fragrance Association, Inc., Washington, D.C. (1982)), which descriptin is incorporated herein by reference.

Nonlimiting examples of cationic deposition polymers for use in the styling shampoo composition include polysaccharide polymers, such as cationic cellulose derivatives. Suitable cationic polysaccharide polymers include those which conform to the formula

wherein A is an anhydroglucose residual group, such as a cellulose anhydroglucose residual; R is an alkylene oxyalkylene, polyoxyalkylene, or hydroxyalkylene group, or combination thereof; R1, R2, and R3 independently are alkyl, aryl, alkylaryl, arylalkyl, alkoxyalkyl, or alkoxyaryl groups, each group containing up to about 18 carbon atoms, and the total number of carbon atoms for each cationic moiety (i.e., the sum of carbon atoms in R1, R2 and R3) preferably being about 20 or less; and X is an anionic counterion as described in hereinbefore.

Preferred cationic cellulose polymers are the salts of hydroxyethyl cellulose reacted with trimethyl ammonium substituted epoxide, referred to in the industry (CTFA) as Polyquaternium 10 which are available from Amerchol Corp. (Edison, NJ, USA) in their Polymer JR and LR series of polymers with the most preferred being JR30M.

Other suitable cationic deposition polymers include cationic guar gum derivatives, such as guar hydroxypropyltrimonium chloride, specific examples of which include the Jaguar series (preferably Jaguar C-17) commercially available from Rhone-Poulenc Incorporated.

The cationic polymers herein are either soluble in the styling shampoo composition, or preferably are soluble in a complex coacervate phase in the styling shampoo composition formed by the cationic deposition polymer and the anionic surfactant component described hereinbefore. Complex coacervates of the cationic deposition polymer can also be formed with other charged materials in the styling shampoo composition.

Coacervate formation is dependent upon a variety of criteria such as molecular weight, component concentration, and ratio of interacting ionic components, ionic strength (including modification of ionic strength, for example, by addition of salts), charge density of the cationic and anionic components, pH, and temperature. Coacervate systems and the effect of these parameters have been described, for example, by J. Caelles, et al., "Anionic and Cationic Compounds in Mixed Systems", Cosmetics & Toiletries, Vol. 106, April 1991, pp 49-54, C. J. van Oss, "Coacervation, Complex-Coacervation and Flocculation", J. Dispersion Science and Technology, Vol. 9 (5,6), 1988-89, pp 561-573, and D. J. Burgess, "Practical Analysis of Complex Coacervate Systems", J. of Colloid and Interface Science, Vol. 140, No. 1, November 1990, pp 227-238, which descriptions are incorporated herein by reference.

It is believed to be particularly advantageous for the cationic deposition polymer to be present in the styling shampoo composition in a coacervate phase, or to form a coacervate phase upon application or rinsing of the shampoo t or from the hair. Complex coacervates are believed to more readily deposit on the hair which results in improved deposition f the styling polymer. Thus, in general, it is preferred that the cationic deposition polymer exist in the styling shampoo composition as a coacervate phase or form a coacervate phase upon dilution. If not already a coacervate in the styling shampoo composition, the cationic deposition polymer will preferably exist in a complex coacervate form in the shampoo upon dilution with water.

Techniques for analysis of formation of complex coacervates are known in the art. For example, microscopic analyses of the styling shampoo compositions, at any chosen stage of dilution, can be utilized to identify whether a coacervate phase has formed. Such coacervate phase will be identifiable as an additional emulsified phase in the composition. The use of dyes can aid in distinguishing the coacervate phase from other insoluble phases dispersed in the styling shampoo composition.

# Cationic Styling Polymer

The styling shampoo compositions of the present invention comprise an organic cationic hair styling polymer suitable for application to human hair or skin, which is used in combination with the cationic deposition polymer described hereinbefore. The polymer can be soluble in water or dispersible in the surfactant components described hereinabove. These styling polymers for use herein are not unduly sticky or tacky to the touch, and provide hair styling benefits such as improved body and longer lasting curl. Concentrations of the styling polymer range from about 0.5% to about 10%, preferably from about 1% to about 8%, more preferably from about 2% to about 6%, and even more preferably from about 2.5% to about 5%, by weight of the composition.

The organic cationic hair styling polymers useful herein have an open chain backbone which contains quaternary ammonium or cationic amino moieties, or combinations thereof. In order to achieve the optimal balance between styling performance and hair feel, the cationic charge density of the hair styling polymer should be less than about 4.75 meq/gram, preferably less than about 3.75 meq/gram, more preferably less than about 3 meq/gram. Furthermore, the charge density should be of a level such that efficient substantivity between the polymer and the hair can be attained, thereby preventing the hair from becoming unduly coated, sticky, or having an undesirably dirty feel. Preferably, the polymer has a cationic charge density of at least about 2 meq/gram, at the pH of the shampoo composition.

A nonlimiting example of suitable cationic hair styling polymers include copolymers of vinyl monomers having cationic amine or quaternary ammonium functionalities with water soluble space monomers such as N-vinyl pyrrolidone.

Other suitable cationic hair styling polymers include those cationic polymers containing or derived from quaternary ammonium monomers, such as vinyl quaternary ammonium monomers having cyclic cationic nitrogen-containing rings such as imidazolium, e.g., alkyl vinyl imidazolium. The alkyl portions of these monomers are preferably lower alkyls such as the C<sub>1</sub>-C<sub>3</sub> alkyls, more preferably C<sub>1</sub> and C<sub>2</sub> alkyls.

Preferred cationic hair styling polymers include copolymers of 1-vinyl-2-pyrrolidone and 1-vinyl-3-methylimidazolium salt (e.g., chloride salt) (referred to in the industry as Polyquaternium-16), such as

those commercially available from BASF Wyandotte Corp. (Parsippany, NJ, USA) under LUVIQUAT tradename (e.g., LUVIQUAT FC 370, and LUVIQUAT FC 550). The most preferred cationic hair styling polymer is LUVIQUAT FC 370.

#### Water

The styling shampoo compositions of the present invention are aqueous systems which comprise from about 27% to about 94.5%, preferably from about 55% to about 85%, more preferably from about 60% to about 75%, of water by weight of the styling shampoo composition.

#### **Optional Components**

The styling shampoo compositions of the present invention may further comprise one or more optional components known or otherwise effective for use in hair care or personal care products, provided that the optional components are physically and chemically compatible with the essential component described herein, or do not otherwise unduly impair product stability, aesthetics or performance. Individual concentrations of such optional components may range from about 0.001% to about 10% by weight of the styling shampoo compositions.

Nonlimiting examples of optional components for use in the styling shampoo composition include perfumes, anti dandruff agents, hair conditioning agents (hydrocarbon oils, fatty esters, silicones), dyes, pearlescent aids, foam boosters, additional surfactants or nonionic cosurfactants, pediculocides, pH adjusting agents, preservatives, proteins, skin active agents, sunscreens, vitamins, and viscosity adjusting agents.

The styling shampoo composition of the present invention preferably further comprises a suspending or thickening agent. Suitable suspending agents for such materials are well known in the art, and include crystalline and polymeric suspending or thickening agents. Crystalline suspending agents are preferred, and include known acyl derivatives and amine oxides, and are described in U.S. Patent 4,741,855, which description is incorporated herein by reference.

Nonlimiting examples of optional polymeric thickening agents for use in the styling shampoo composition include carboxyvinyl polymers, cellulose ethers, guar gum, polyvinyl alcohol, polyvinyl pyrrolidone, hydroxypropyl guar gum, starch and starch derivatives, and xantham gum. Suspending or thickening agents are described in U.S. Patent 2,798,053, U.S. Patent 4,686,254, U.S. Patent 4,788,006, and U.S. Patent 5,275,761, which descriptions are incorporated herein by reference. The optional suspending or thickening agents are described in more detail hereinafter.

The styling shampoo composition of the present invention may further comprise a silicone hair conditioning agent, preferably a silicone hair conditioning agent in combination with an optional suspending agent for the silicone. The silicone hair conditioning agent is preferably non volatile, and is preferably present in the styling shampoo composition at concentrations ranging from about 0.01% to about 10% by weight of the styling shampoo composition. Nonlimiting examples of suitable silicone hair conditioning agents, and optional suspending agents for the silicone, are described in U.S. Reissue Patent

34,584 (Grote et al.), U.S. Patents 5,104,646 (Bolich Jr. et al.), U.S. Patent 5,106,609 (Bolich Jr. et al.), which descriptions are incorporated herein by reference. The optional silicone hair conditioning agent, and optional suspending agents for the optional silicone, are described in more detail hereinafter

### Optional Silicone Hair Conditioning Agent

The styling shampoo compositions of the present invention may further comprise an optional silicone hair conditioning agent at concentrations effective to provide hair conditioning benefits. Such concentrations range from about 0.01% to about 10%, preferably from about 0.1% to about 5%, more preferably from about 0.15% to about 3%, most preferably from about 0.2% to about 1%, by weight of the styling shampoo compositions.

The optional silicone hair conditioning agents are insoluble in the styling shampoo compositions, and are preferably nonvolatile. Typically it will be intermixed in the styling shampoo composition so as to be in the form of a separate, discontinuous phase of dispersed, insoluble particles, also referred to as droplets. These droplets are typically suspended with an optional suspending agent described hereinafter. The optional silicone hair conditioning agent phase will comprise a silicone fluid hair conditioning agent such as a silicone fluid and can also comprise other ingredients, such as a silicone resin to improve silicone fluid deposition efficiency or enhance glossiness of the hair (especially when high refractive index (e.g. above about 1.46)) silicone conditioning agents are used (e.g. highly phenylated silicones).

The optional silicone hair conditioning agent phase may comprise volatile silicone, nonvolatile silicone, or combinations thereof. Typically, if volatile silicones are present, it will be incidental to their use as a solvent or carrier for commercially available forms of nonvolatile silicone materials ingredients, such as silicone gums and resins.

The optional silicone hair conditioning agents for use in the styling shampoo compositions preferably have a viscosity of from about 20 to about 2,000,000 centistokes, more preferably from about 1,000 to about 1,800,000 centistokes, even more preferably from about 50,000 to about 1,500,000 centistokes, most preferably from about 100,000 to about 1,500,000 centistokes, as measured at 25°C.

Optional silicone fluids include silicone oils which are flowable silicone materials having a viscosity of less than 1,000,000 centistokes, preferably between about 5 and 1,000,000 centistokes, more preferably between about 10 and about 100,000 centistokes, at 25°C. Suitable silicone oils include polyalkyl siloxanes, polyaryl siloxanes, polyalkylaryl siloxanes, polyether siloxane copolymers, and combinations thereof. Other insoluble, nonvolatile silicone fluids having hair conditioning properties can also be used.

Optional silicone oils include polyalkyl or polyaryl siloxanes which conform to the following formula (I)

where R is aliphatic, preferably alkyl or alkenyl, or aryl, R can be substituted or unsubstituted, and x is an integer from 1 to about 8,000. Suitable unsubstituted R groups include alkoxy, aryloxy, arylalkyl, arylalkenyl, alkylamine, and ether-substituted, hydroxyl-substituted, and halogen-substituted aliphatic and aryl groups. Suitable R groups also include cationic argines and quaternary aramonium groups.

The aliphatic or aryl groups substituted on the siloxane chain may have any structure so long as the resulting silicones remain fluid at room temperature, are hydrophobic, are neither irritating, toxic nor otherwise harmful when applied to the hair, are compatible with the other components of the styling shampoo compositions, are chemically stable under normal use and storage conditions, are insoluble in the styling shampoo compositions herein, and are capable of being deposited on and conditioning the hair.

The two R groups on the silicon atom of each monomeric silicone unit may represent the same or different groups. Preferably, the two R groups represent the same group.

Preferred alkyl and alkenyl substituents are  $C_1$ - $C_5$  alkyls and alkenyls, more preferably from  $C_1$ - $C_4$ , most preferably from  $C_1$ - $C_2$ . The aliphatic portions of other alkyl-, alkenyl-, or alkynyl-containing groups (such as alkoxy, arylalkyl, and alkylamino) can be straight or branched chains and preferably have from one to five carbon atoms, more preferably from one to four carbon atoms, even more preferably from one to two carbon atoms. As discussed above, the R substituents hereof can also contain amino functionalities, e.g. alkamino groups, which can be primary, secondary or tertiary amines or quaternary ammonium. These include mono-, di- and tri- alkylamino and alkoxyamino groups wherein the aliphatic portion chain length is preferably as described above. The R substituents can also be substituted with other groups, such as halogens (e.g. chloride, fluoride, and bromide), halogenated aliphatic or aryl groups, and hydroxy (e.g. hydroxy substituted aliphatic groups). Suitable halogenated R groups could include, for example, iri-halogenated (preferably fluoro) alkyl groups such as  $-R^1$ - $C(F)_3$ , wherein  $R^1$  is  $C_1$ - $C_3$  alkyl. Examples of such polysiloxanes include polymethyl -3,3,3 trifluoropropylsiloxane.

Suitable R groups include methyl, ethyl, propyl, phenyl, methylphenyl and phenylmethyl. The preferred silicones are polydimethyl siloxane, polydiethylsiloxane, and polymethylphenylsiloxane. Polydimethylsiloxane is especially preferred. Other suitable R groups include methyl, methoxy, ethoxy, propoxy, and aryloxy. The three R groups on the end caps of the silicone may also represent the same or different groups.

The nonvolatile polyalkylsiloxane fluids that may be used include, for example, polydimethylsiloxanes. These siloxanes are available, for example, from the General Electric Company in their Viscasil R and SF 96 series, and fr m Dow Corning in their Dow Corning 200 series.

The polyalkylaryl siloxane fluids that may be used, also include, for example, polymethylphenylsiloxanes. These siloxanes are available, for example, from the General Electric Company as SF 1075 methyl phenyl fluid or from Dow Corning as 556 Cosmetic Grade Fluid.

The polyether siloxane copolymers that may be used include, for example, a polypropylene oxide modified polydimethylsiloxane (e.g., Dow Coming DC-1248) although ethylene oxide or mixtures of ethylene oxide and propylene oxide may also be used. The ethylene oxide and polypropylene oxide concentrations must be sufficiently low to prevent solubility in water and the composition hereof.

Suitable alkylamino substituted silicones include those which conform to the following structure

(II) is a function of the median and the man in the conjugate of the median co

wherein x and y are integers. This polymer is also known as "amodimethicone".

Suitable cationic silicone fluids include those which conform to the formula (III)

(R<sub>1</sub>)<sub>a</sub>G<sub>3-a</sub>-Si-(-OSiG<sub>2</sub>)<sub>n</sub>-(-OSiG<sub>b</sub>(R<sub>1</sub>)<sub>2-b</sub>)<sub>m</sub>-O-SiG<sub>3-a</sub>(R<sub>1</sub>)<sub>a</sub>, wherein G is selected from the group consisting of hydrogen, phenyl, hydroxy, C<sub>1</sub>-C<sub>8</sub> alkyl and preferably methyl; a is 0 or an integer having a value from 1 to 3, preferably 0; b is 0 or 1, preferably 1; the sum n+m is a number from 1 to 2,000 and preferably from 50 to 150, n being able to denote a number from 0 to 1,999 and preferably from 49 to 149 and m being able to denote an integer from 1 to 2,000 and preferably from 1 to 10; R<sub>1</sub> is a monovalent radical conforming to the formula CqH<sub>2</sub>qL in which q is an integer having a value of from 2 to 8 and L is selected from the following groups:

in which R<sub>2</sub> is selected from the group consisting of hydrogen, phenyl, benzyl, a saturated hydrocarbon radical, preferably an alkyl radical containing from 1 to 20 carbon atoms, and A is a halide ion.

An especially preferred cationic silicone corresponding to formula (III) is the polymer known as "trimethylsilylamodimethicone", of formula (IV):

A first settle of Linear Control of the party of the control of the

Other silicone cationic polymers which can be used in the styling shampoo compositions are represented by the formula (V):

where  $R^3$  denotes a monovalent hydrocarbon radical having from 1 to 18 carbon atoms, preferably an alkyl or alkenyl radical such as methyl;  $R_4$  denotes a hydrocarbon radical, preferably a  $C_1$ - $C_{18}$  alkylene radical or a  $C_1$ - $C_{18}$ , and more preferably  $C_1$ - $C_8$ , alkyleneoxy radical; Q is a halide ion, preferably chloride; r denotes an average statistical value from 2 to 20, preferably from 2 to 8; s denotes an average statistical value from 20 to 50. A preferred polymer of this class is available from Union Carbide under the name "UCAR SILICONE ALE 56."

Other optional silicone fluids are the insoluble silicone gums. These gums are polyorganosiloxane materials having a viscosity at 25°C of greater than or equal to 1,000,000 centistokes. Silicone gums are described in U.S. Patent 4,152,416; Noll and Walter, Chemistry and Technology of Silicones, New York: Academic Press 1968; and in General Electric Silicone Rubber Product Data Sheets SE 30, SE 33, SE 54 and SE 76, all of which are incorporated herein by reference. The silicone gums will typically have a mass molecular weight in excess of about 200,000, generally between about 200,000 and about 1,000,000, specific examples of which include polydimethylsiloxane, (polydimethylsiloxane) (methylvinylsiloxane) copolymer, poly(dimethylsiloxane) (diphenyl siloxane)(methylvinylsiloxane) copolymer, and mixtures thereof.

Another category of nonvolatile, insoluble silicone fluid conditioning agents are the high refractive index silicones, having a refractive index of at least about 1.46, preferably at least about 1.48, more preferably at least about 1.52, most preferably at least about 1.55. The refractive index of the

polysil xane fluid will generally be less than about 1.70, typically less than about 1.60. In this context, polysiloxane "fluid" includes oils as well as gums.

The high refractive index polysiloxane fluid includes those represented by general Formula (I) above, as well as cyclic polysiloxanes such as those represented by Formula (VI) below:

wherein R is as defined above, n is from about 3 to about 7, preferably from 3 to 5.

The high refractive index polysiloxane fluids contain a sufficient amount of aryl-containing R substituents to increase the refractive index to the desired level, which is described above. In addition, R and n must be selected so that the material is nonvolatile, as defined above.

Aryl-containing substituents contain alicyclic and heterocyclic five and six membered aryl rings, and substituents containing fused five or six membered rings. The aryl rings themselves can be substituted or unsubstituted. Substituents include aliphatic substituents, and can also include alkoxy substituents, acyl substituents, ketones, halogens (e.g., Cl and Br), amines, etc. Exemplary aryl-containing groups include substituted and unsubstituted arenes, such as phenyl, and phenyl derivatives such as phenyls with  $C_1$ - $C_5$  alkyl or alkenyl substituents, e.g., allylphenyl, methyl phenyl and ethyl phenyl, vinyl phenyls such as styrenyl, and phenyl alkynes (e.g. phenyl  $C_2$ - $C_4$  alkynes). Heterocyclic aryl groups include substituents derived from furan, imidazole, pyrrole, pyridine, etc. Fused aryl ring substituents include, for example, napthalene, coumarin, and purine.

In general, the high refractive index polysiloxane fluids will have a degree of aryl-containing substituents of at least about 15%, preferably at least about 20%, more preferably at least about 25%, even more preferably at least about 35%, most preferably at least about 50%. Typically, although it is not intended to necessarily limit the invention, the degree of aryl substitution will be less than about 90%, more generally less than about 85%, preferably from about 55% to about 80%.

The polysiloxane fluids are also characterized by relatively high surface tensions as a result of their aryl substitution. In general, the polysiloxane fluids hereof will have a surface tension of at least about 24 dynes/cm<sup>2</sup>, typically at least about 27 dynes/cm<sup>2</sup>. Surface tension, for purposes hereof, is measured by a de Nouy ring tensiometer according to Dow Corning Corporate Test Method CTM 0461, November 23, 1971. Changes in surface tension can be measured according to the above test method or according to ASTM Method D 1331.

Preferred high refractive index polysiloxane fluids have a combination of phenyl or phenyl derivative substituents (preferably phenyl), with alkyl substituents, preferably  $C_1$ - $C_4$  alkyl (most preferably methyl), hydroxy,  $C_1$ - $C_4$  alkylamino (especially -R<sup>1</sup>NHR<sup>2</sup>NH2 where each R<sup>1</sup> and R<sup>2</sup>

independently is a C<sub>1</sub>-C<sub>3</sub> alkyl, alkenyl, and/or alkoxy. High refractive index polysiloxanes are available from Dow Corning Corporation (Midland, Michigan, U.S.A.) Huls America (Piscataway, New Jersey, U.S.A.), and General Electric Silicones (Waterford, New York, U.S.A.).

References disclosing examples of some suitable silicone fluids for use in the styling shampoo compositions include U.S. Patent 2,826,551, U.S. Patent 3,964,500, U.S. Patent 4,364,837, British Patent 849,433, and Silicon Compounds, Petrarch Systems, Inc. (1984), all of which are incorporated herein by reference.

Silicone resins can be included in the silicone conditioning agent. These resins are highly crosslinked polymeric siloxane systems. The crosslinking is introduced through the incorporation of trifunctional and tetrafunctional silanes with monofunctional or difunctional, or both, silanes during manufacture of the silicone resin. As is well understood in the art, the degree of crosslinking that is required in order to result in a silicone resin will vary according to the specific silane units incorporated into the silicone resin. In general, silicone materials which have a sufficient level of trifunctional and tetrafunctional siloxane monomer units (and hence, a sufficient level of crosslinking) such that they dry down to a rigid, or hard, film are considered to be silicone resins. The ratio of oxygen atoms to silicon atoms is indicative of the level of crosslinking in a particular silicone material. Silicone materials which have at least about 1.1 oxygen atoms per silicon atom will generally be silicone resins herein. Preferably, the ratio of oxygen:silicon atoms is at least about 1.2:1.0. Silanes used in the manufacture of silicone resins include monomethyl-, dimethyl-, trimethyl-, monophenyl-, diphenyl-, methylphenyl-, monovinyl-, and methylvinyl-chlorosilanes, and tetrachlorosilane, with the methyl-substituted silanes being most commonly utilized. Preferred resins are offered by General Electric as GE SS4230 and SS4267. Commercially available silicone resins will generally be supplied in a dissolved form in a low viscosity volatile or nonvolatile silicone fluid. The silicone resins for use herein should be supplied and incorporated into the present compositions in such dissolved form, as will be readily apparent to those skilled in the art.

Background material on silicones including sections discussing silicone fluids, gums, and resins, as well as manufacture of silicones, can be found in Encyclopedia of Polymer Science and Engineering, Volume 15, Second Edition, pp 204-308, John Wiley & Sons, Inc., 1989, incorporated herein by reference.

Silicone materials and silicone resins in particular, can conveniently be identified according to a shorthand nomenclature system well known to those skilled in the art as "MDTQ" nomenclature. Under this system, the silicone is described according to presence of various siloxane monomer units which make up the silicone. Briefly, the symbol M denotes the monofunctional unit (CH<sub>3</sub>)<sub>3</sub>SiO<sub>.5</sub>; D denotes the difunctional unit (CH<sub>3</sub>)<sub>2</sub>SiO; T denotes the trifunctional unit (CH<sub>3</sub>)SiO<sub>1.5</sub>; and Q denotes the quadrior tetra-functional unit SiO<sub>2</sub>. Primes of the unit symbols, e.g., M', D', T', and Q' denote substituents ther than methyl, and must be specifically defined for each occurrence. Typical alternate substituents include groups such as vinyl, phenyls, amines, hydroxyls, etc. The molar ratios of the various units, either in

terms of subscripts to the symbols indicating the total number of each type of unit in the silicone (or an average there f) or as specifically indicated ratios in combination with molecular weight complete the description of the silicone material under the MDTQ system. Higher relative molar amounts of T, Q, T and/or Q' to D, D', M and/or M' in a silicone resin is indicative of higher levels of crosslinking. As discussed before, however, the overall level of crosslinking can also be indicated by the oxygen to silicon ratio.

The silicone resins for use herein which are preferred are MQ, MT, MTQ, MDT and MDTQ resins. Thus, the preferred silicone substituent is methyl. Especially preferred are MQ resins wherein the M:Q ratio is from about 0.5:1.0 to about 1.5:1.0 and the average molecular weight of the resin is from about 1000 to about 10,000.

The weight ratio of the nonvolatile silicone fluid, having refractive index below 1.46, to the silicone resin component, when used, is preferably from about 4:1 to about 400:1, preferably this ratio is from about 9:1 to about 200:1, more preferably from about 19:1 to about 100:1, particularly when the silicone fluid component is a polydimethylsiloxane fluid or a mixture of polydimethylsiloxane fluid and polydimethylsiloxane gum as described above. Insofar as the silicone resin forms a part of the same phase in the compositions hereof as the silicone fluid, i.e. the conditioning active, the sum of the fluid and resin should be included in determining the level of silicone conditioning agent in the composition.

### **Optional Suspending Agent**

The styling shampoo compositions of the present invention may further comprise a suspending agent at concentrations effective for suspending the optional silicone hair conditioning agent, or other water-insoluble material, in dispersed form in the styling shampoo compositions. Such concentrations range from about 0.1% to about 10%, preferably from about 0.3% to about 5.0%, by weight of the styling shampoo compositions.

Optional suspending agents include crystalline suspending agents that can be categorized as acyl derivatives, long chain amine oxides, or combinations thereof, concentrations of which range from about 0.1% to about 5.0%, preferably from about 0.5% to about 3.0%, by weight of the styling shampoo compositions. When used in the styling shampoo compositions, these suspending agents are present in crystalline form. These suspending agents are described in U.S. Patent 4,741,855, which description is incorporated herein by reference. These preferred suspending agents include ethylene glycol esters of fatty acids preferably having from about 16 to about 22 carbon atoms. More preferred are the ethylene glycol stearates, both mono and distearate, but particularly the distearate containing less than about 7% of the mono stearate. Other suitable suspending agents include alkanol amides of fatty acids, preferably having from about 16 to about 22 carbon atoms, more preferably about 16 to 18 carbon atoms, preferred examples of which include stearic monoethanolamide, stearic diethanolamide, stearic monoisopropanolamide and stearic monoethanolamide stearate. Other long chain acyl derivatives include long chain esters of long chain fatty acids (e.g., stearyl stearate, cetyl palmitate, etc.); glyceryl esters (e.g.,

glyceryl distearate) and I ng chain esters of long chain alkanol amides (e.g., stearamide diethanolamide distearate, stearamide monoethanolamide stearate). Long chain acyl derivatives, ethylene glycol esters of long chain carboxylic acids, long chain amine oxides, and alkanol amides of long chain carboxylic acids in addition to the preferred materials listed above may be used as suspending agents. For example, it is contemplated that suspending agents with long chain hydrocarbyls having C<sub>8</sub>-C<sub>22</sub> chains may be used.

Other long chain acyl derivatives suitable for use as suspending agents include N,N-dihydrocarbyl amido benzoic acid and soluble salts thereof (e.g., Na, K), particularly N,N-di(hydrogenated)  $C_{16}$ ,  $C_{18}$  and tallow amido benzoic acid species of this family, which are commercially available from Stepan Company (Northfield, Illinois, USA).

Examples of suitable long chain amine oxides for use as suspending agents include alkyl ( $C_{16}$ - $C_{22}$ ) dimethyl amine oxides, e.g., stearyl dimethyl amine oxide.

Other suitable suspending agents include xanthan gum at concentrations ranging from about 0.3% to about 3%, preferably from about 0.4% to about 1.2%, by weight of the styling shampoo compositions. The use of xanthan gum as a suspending agent in silicone containing shampoo compositions is described, for example, in U.S. Patent 4,788,006, which description is incorporated herein by reference. Combinations of long chain acyl derivatives and xanthan gum may also be used as a suspending agent in the styling shampoo compositions. Such combinations are described in U.S. Patent 4,704,272, which description is incorporated herein by reference.

Other suitable suspending agents include carboxyvinyl polymers. Preferred among these polymers are the copolymers of acrylic acid crosslinked with polyallylsucrose as described in U.S. Patent 2,798,053, which description is incorporated herein by reference. Examples of these polymers include Carbopol 934, 940, 941, and 956, available from B. F. Goodrich Company.

Other suitable suspending agents include primary amines having a fatty alkyl moiety having at least about 16 carbon atoms, examples of which include palmitamine or stearamine, and secondary amines having two fatty alkyl moieties each having at least about 12 carbon atoms, examples of which include dipalmitoylamine or di(hydrogenated tallow)amine. Still other suitable suspending agents include di(hydrogenated tallow)phthalic acid amide, and crosslinked maleic anhydride-methyl vinyl ether copolymer.

Other suitable suspending agents may be used in the styling shampoo compositions, including those that can impart a gel-like viscosity to the composition, such as water soluble or colloidally water soluble polymers like cellulose ethers (e.g., methylcellulose, hydroxybutyl methylcellulose, hyroxypropylcellulose, hydroxypropyl methylcellulose, hydroxyethyl ethylcellulose and hydoxxethylcellul se), guar gum, polyvinyl alcohol, polyvinyl pyrrolidone, hydroxypropyl guar gum, starch and starch derivatives, and other thickeners, viscosity modifiers, gelling agents, etc. Mixtures of these materials can also be used.

#### M thod of Use

The styling shampoo compositions of the present invention are used in a conventional manner for cleansing and styling hair. An effective amount of the composition for cleansing and styling the hair is applied to the hair, that has preferably been wetted with water, and is then rinsed off. Such effective amounts preferably range from about 1gm to about 50gm, more preferably from about 3gm to about 20gm. Application to the hair typically includes working the composition through the hair such that most or all of the hair is contacted with the composition.

This method for cleansing and styling the hair comprises the steps of a) wetting the hair with water, b) applying an effective amount of the styling shampoo composition to the hair, c) shampooing the hair with the composition, and d) rinsing the composition from the hair with water. These steps can be repeated as many times as desired to achieve the cleansing and styling benefit desired. The method is preferably employed daily, every other day, or every third day, to provide and maintain the hair cleansing and styling performance described herein.

#### Examples

The following examples further describe and demonstrate embodiments within the scope of the present invention. The examples are given solely for the purpose of illustration and are not to be construed as limitations of the present invention, as many variations thereof are possible without departing from the spirit and scope of the invention. The exemplified embodiments of the styling shampoo composition of the present invention provide both conditioning and styling performance without leaving the hair feeling unduly coated, dirty, sticky, or tacky to the touch. Ingredients are herein identified by chemical, trade, of CTFA name.

The styling shampoo compositions illustrated in Examples I-V are prepared by conventional formulation and mixing techniques, an example of which is set forth hereinbelow. All exemplified amounts are listed as weight percents and exclude minor materials such as diluents, filler, and so forth, unless otherwise specified.

### **Preparation**

The styling shampoo compositions of the present invention may be prepared using conventional formulation and mixing techniques. The solid components are dispersed directly into a premix of the surfactants, or some portion of the surfactants which has been heated to melt the solid components, e.g., about 72°C. This mixture is then pumped through a high shear mill and cooled, and then the remaining components, including the cationic deposition polymer and the cationic styling polymer, are mixed in. The composition should have a final viscosity of from about 2,000 to about 15,000 cps, preferably from about 4,000 to about 10,000 cps. The viscosity of the composition can be adjusted using sodium chloride or ammonium xylenesulfonate as needed.

Component of Chamber 1 2 to 4 to 1 4 to 1 4 to 1 4 to 1	4. 36. 6	V	Veight %	6	
The second of th	I	II	III	IV	V
Ammonium Laureth Sulfate	9.5	9.0	9.3	9.3	9.5
Ammonium Lauryl Sulfate	1.0	3.0			1.0
Lauroamphoacetate  Consmidentantel Retains FR (4)	7.5	6.0			7.5
Cocamidopropyl Betaine FB (4)			4.7	4.7	
Polyquaternium-16 (Luviquat FC 370) (1)	2.0	3.0	3.0	2.0	3.0
Monosodium Phosphate	0.1	0.1	0.1	0.1	0.1
Disodium Phosphate	0.2	0.2	0.2	0.2	0.2
Glycol Distearate	2.0	2.0	2.0	2.0	2.0
Cocomonoethanol amide	0.6	0.6	0.6	0.6	0.6
Fragrance	1.0	1.0	1.0	1.0	1.0
Cetyl Alcohol	0.07		0.42	0.42	0.14
Stearyl Alcohol	0.03		0.18	0.18	0.06
PEG-150 Pentaerythrityl Tetrastearate	0.1	0.15		0.08	0.20
Polyquaternium 10 (JR30M) (2)	0.3		0.3		0.2
Polyquaternium 10 (JR400) (2)				0.4	***
Guar Hydroxypropyltrimonium Chloride (Jaguar C-17) (3)		0.3			
Dimethicone A A A A A A A A A A A A A A A A A A A	0.25		Line <del>yan</del> a ini	—	
DMDM Hydantoin	0.2	0.2	0.2	0.2	0.2
Water	qs 100	qs 100	qs 100	qs 100	qs 100

CONTRACTOR FOR CALL RIMP IN 125 TRAINS

A LOS DE ARTS OF THE SECOND STATE OF THE SECOND SECOND

in a structure of great fill a contribution where we are both the substitute of the purpose a the control of the winder of the first area of the area of the series of the control of the cont

the control of the probability to the last the property and all the set, the second term

The first of the country of the first specific that the section of The strip of the originative of the strip of

さい つんまじょう かっとう かんりょう

<sup>(1)</sup> Available from BASF (Ludwigshafen, Germany)

<sup>(2)</sup> Available from Amerchol Corp. (Edison, NJ, USA)

<sup>(3)</sup> Available from Rhone-Poulenc (Cranbury, NJ, USA)
(4) Available from Goldschmidt (Hopewell, Virginia, USA) The Art of the Dr. Ingramma have a consider the file

#### What is claimed is:

- 1. A styling shampoo composition comprising:
  - (a) from 5% to 50% by weight of a surfactant component selected from the group consisting of a combination of an anionic surfactant and an amphoteric surfactant, and a combination of an anionic surfactant and a zwitterionic surfactant;
  - (b) from 0.025% to 3% by weight of a cationic deposition polymer having a cationic charge density of from 0.2 meq/gram to 2 meq/gram and which is selected from the group consisting of cationic cellulose polymers, cationic guar gum derivatives, and mixtures thereof;
  - (c) from 0.5% to 10% by weight of an organic cationic hair styling polymer having a cationic charge density of greater than 2 meq/gram to less than 4.75 meq/gram; and
  - (d) from 27% to 94.5% by weight water.
- 2. The composition of Claim 1 wherein the anionic surfactant is selected from the group consisting of ammonium lauryl sulfate, ammonium laureth sulfate, alkyl glyceryl ether sulfonate, and mixtures thereof; the amphoteric surfactant is selected from the group consisting of lauroamphoacetate, lauroamphodiacetate, cocoamphoacetate, cocoamphodiacetate, and mixtures thereof; and the zwitterionic surfactant is a betaine surfactant.
- 3. The composition of Claim 1 or 2 wherein the betaine surfactant is cocoamidopropyl betaine.
- 4. A styling shampoo composition comprising:
  - (a) from 5% to 50% by weight of a surfactant combination of ammonium laureth sulfate and cocoamidopropyl betaine having a weight ratio of ammonium laureth sulfate to cocoamidopropyl betaine of from 1.5:1 to 10:1;
  - (b) from 0.025% to 3% by weight of a cationic deposition polymer having a cationic charge density of from 0.2 meq/gram to 2 meq/gram and which is selected from the group consisting of cationic cellulose polymers, cationic guar gum derivatives, and mixtures thereof;

- (c) from 0.5% to 10% by weight of Polyquaternium-16 as an organic cationic hair styling polymer having a charge density of greater than 2 meq/gram to less than 4.75 meq/gram; and
- (d) from 27% to 94.5% by weight of water.
- 5. The composition of any one of the preceding claims wherein the organic cationic hair styling polymer is a copolymer of 30% vinylimidazole and 70% vinyl pyrrolidone.
- 6. The composition of any one of the preceding claims wherein the cationic cellulose polymer is Polyquaternium-10, and the guar gum derivative is guar hydroxypropyltrimonium chloride.
- 7. The composition of any one of the preceding claims wherein the composition further comprises a non-volatile hair conditioning agent selected from the group consisting of polyarylsiloxanes, polyalkylsiloxanes, polyalkylsiloxanes, derivatives thereof, and mixtures thereof.
- 8. The composition of Claim 7 wherein the composition comprises from 0.15% to 3% by weight of a non-volatile polydimethylsiloxane as the hair conditioning agent.
- 9. A method for cleansing and styling the hair, which method comprises the steps of:
  (a)wetting the hair with water,
  - (b) applying from 1 gram to 50 grams of the composition of Claim 1 to the hair,
  - (c) shampooing the hair with the composition, and
  - (d) rinsing the composition from the hair using water.
- 10. A method for cleansing and styling the hair, which method comprises the steps of:
  (a) wetting the hair with water,
  - (b) applying from 1 gram to 50 grams of the composition of Claim 4 to the hair,
  - (c)shampooing the hair with the composition, and
    - (d) rinsing the composition from the hair using water.

PCT/IB 98/00651

A. CLASSII IPC 6	FICATION OF SUBJECT MATTER A61K7/06 A61K7/50	
According to	) International Patent Classification(IPC) or to both national classificat	ion and IPC
	SEARCHED	
	cumentation searched (classification system followed by classification	n symbols)
IPC 6	A61K	
Documentat	ion searched other than minimum documentation to the extent that suc	ch documents are included in the fields searched
٠.	stands at the first of the company of the	in the second of
Electronic d	ata base consulted during the international search (name of data basi	and, where practical, search terms used)
	over the presentation of the second of the	ABBO SPORT ALBERT DAILS TO THE SPORT OF THE
C. DOCUM	ENTS CONSIDERED TO BE RELEVANT AND 1986 (4)	to the state of th
Category *	Citation of document, with indication, where appropriate, of the relev	vant passages Relevant to claim No.
X	US 5 580 494 A (SANDHU SUKHVINDER AL) 3 December 1996 see column 2, line 46 - line 64 see column 3, line 10 - line 14 see column 4, line 46 - line 50	re son enonge e in grand per en
<b>X</b>	see column 4, line 66 - line 67 see example 7 WO 94 06403 A (COLGATE PALMOLIVE March 1994	Committee to the second
	see page 4, line 17 - line 18 see page 10, line 13 - line 16 see claims 1,15	THE WILL HAVE A STORY
. :	r i ka se e base <del>at </del> demons	A transfer out to the state of
		y — Constitution of the Europe of the Constitution of the Constitu
•	r di kommunik jerondi okub jerok	
•	177 January Barangan	
		, , , ,
	han a san a sa	A STATE OF THE STA
X Furt	her documents are listed in the continuation of box C.	Patent family members are listed in annex.
"A" docume consider filling of the which critatio "O" docume other "P" docume.	ent defining the general state of the art which is not dered to be of particular relevance document but published on or after the international date ant which may throw doubts on priority claim(s) or is cited to establish the publication date of another no rother special reason (as specified) ent referring to an oral disclosure, use, exhibition or means ent published prior to the international filling date but	"T" later document published after the international filling date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention.  "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone.  "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documenta, such combination being obvious to a person skilled in the art.  "3." document member of the same patent family
Date of the	actual completion of the international search	Date of mailing of the international search report
2	8 August 1998	14/09/1998
Name and I	mailing address of the ISA  European Patent Office, P.B. 5818 Patentlaan 2  NL - 2280 HV Rijswijk  Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 440-3016	Authorized officer Pelli Wablat, B

In ational Application No
PCT/IB 98/00651

July 1997 see page 8, line 28 - line 30 see page 9, line 16 - line 20 see page 10 see examples 1-12 see claims 1-3  WO 97 26860 A (JOHNSON & JOHNSON CONSUMER) 31 July 1997 see page 13, line 23 - line 26 see page 23; examples 4,5 see page 24; examples 7,8 see page 31; examples 45,46,48,50 see page 32; examples 51-54 see page 33; example 5  US 5 391 368 A (GERSTEIN TERRY) 21 February 1995 see the whole document  PATENT ABSTRACTS OF JAPAN vol. 018, no. 191 (C-1186), 4 April 1994 & JP 05 345708 A (KAO CORP), 27 December 1993, see abstract	1-3,9 1-3,5,9 1-3,6,9
WO 97 29736 A (UNILEVER PLC; UNILEVER NV (NL)) 21 August 1997 see page 17, paragraph 3 see page 19; examples see claims 1,2  WO 97 25975 A (COLGATE PALMOLIVE CO) 24 July 1997 see page 8, line 28 - line 30 see page 9, line 16 - line 20 see page 10 see examples 1-12 see claims 1-3  WO 97 26860 A (JOHNSON & JOHNSON CONSUMER) 31 July 1997 see page 13, line 23 - line 26 see page 23; examples 4,5 see page 24; examples 7,8 see page 24; examples 7,8 see page 31; examples 45,46,48,50 see page 32; examples 51-54 see page 33; example 5  US 5 391 368 A (GERSTEIN TERRY) 21 February 1995 see the whole document  PATENT ABSTRACTS OF JAPAN vol. 018, no. 191 (C-1186), 4 April 1994 & JP 05 345708 A (KAO CORP), 27 December 1993, see abstract	1-3,9
(NL)) 21 August 1997 see page 17, paragraph 3 see page 19; examples see claims 1,2  X W0 97 25975 A (COLGATE PALMOLIVE CO) 24 July 1997 see page 8, line 28 - line 30 see page 9, line 16 - line 20 see page 10 see examples 1-12 see claims 1-3  X W0 97 26860 A (JOHNSON & JOHNSON CONSUMER) 31 July 1997 see page 13, line 23 - line 26 see page 23; examples 4,5 see page 24; examples 7,8 see page 31; examples 45,46,48,50 see page 32; examples 51-54 see page 33; example 5  US 5 391 368 A (GERSTEIN TERRY) 21 February 1995 see the whole document  PATENT ABSTRACTS OF JAPAN vol. 018, no. 191 (C-1186), 4 April 1994 & JP 05 345708 A (KAO CORP), 27 December 1993, see abstract	1,3,5,9
July 1997 see page 8, line 28 - line 30 see page 9, line 16 - line 20 see page 10 see examples 1-12 see claims 1-3  WO 97 26860 A (JOHNSON & JOHNSON CONSUMER) 31 July 1997 see page 13, line 23 - line 26 see page 23; examples 4,5 see page 24; examples 7,8 see page 31; examples 45,46,48,50 see page 32: examples 51-54 see page 33; example 5  US 5 391 368 A (GERSTEIN TERRY) 21 February 1995 see the whole document  PATENT ABSTRACTS OF JAPAN vol. 018, no. 191 (C-1186), 4 April 1994 & JP 05 345708 A (KAO CORP), 27 December 1993, see abstract	1-3,6,9
WO 97 26860 A (JOHNSON & JOHNSON CONSUMER) 31 July 1997 see page 13, line 23 - line 26 see page 23; examples 4,5 see page 24; examples 7,8 see page 31; examples 45,46,48,50 see page 32; examples 51-54 see page 33; example 5  US 5 391 368 A (GERSTEIN TERRY) 21 February 1995 see the whole document  PATENT ABSTRACTS OF JAPAN vol. 018, no. 191 (C-1186), 4 April 1994 & JP 05 345708 A (KAO CORP), 27 December 1993, see abstract	1-10
February 1995 see the whole document  PATENT ABSTRACTS OF JAPAN vol. 018, no. 191 (C-1186), 4 April 1994 & JP 05 345708 A (KAO CORP), 27 December 1993, see abstract	
vol. 018, no. 191 (C-1186), 4 April 1994 & JP 05 345708 A (KAO CORP), 27 December 1993, see abstract	1-10
WO 92 10162 A (PROCTER & GAMBLE) 25 June 1992 see the whole document	1-3,5-9
FROSCH FRANZ: PARFUMS, COSMET., AROMES, vol. 83, 1988, pages 99-102, XP002074402 see the whole document	1-5,9,10
WO 98 18433 A (PROCTER & GAMBLE) 7 May 1998 see examples 9,14	1-10

Information on patent family members

National Application No

Patent document cited in search report   Publication date	US 5580494 A	date 03-12-1996	US US AU CN MX WO ZA AT AU CA CN DE DE DE DE P FI GR HU JP	52137 50512 49283 10898 93057 94064 93069 1181 1256 6401 57556 20193 10554 690167 690212 6904134 04105 04105 04105 04105 04105 901004	16 A 50 A 93 A 30 A 46 A 09 A 65 T 43 B 90 A 45 D 15 D 167 A 167 A 167 A 167 A 168 A 168 A 168 B	25 24 12 27 31 31 20 15 15 19 10 23 23 24 27 20 27 27 20 20 27 27 20 20 20 20 20 20 20 20 20 20 20 20 20	date  -05-1993 -09-1991 -04-1994 -05-1994 -05-1994 -03-1995 -02-1995 -08-1995 -08-1991 3-03-1991 3-03-1995 7-07-1995 7-07-1995 7-07-1991 3-03-1991 3-03-1991 3-03-1991 3-03-1991 3-03-1991 3-03-1991 3-03-1991 3-03-1991 3-03-1991 3-03-1991 3-03-1991 3-03-1991 3-03-1991 3-03-1991 3-03-1991 3-03-1991 3-03-1991 3-03-1991
US 5051250 A 24-09-1991 AU 4928393 A 12-04-1994 CN 1089830 A 27-07-1994 MX 9305746 A 31-05-1994 W0 9406409 A 31-03-1994 ZA 9306928 A 20-03-1995 AT 118165 T 15-02-1995 AT 125689 T 15-08-1995 AU 640143 B 19-08-1993 AU 640143 B 19-08-1993 AU 640143 B 19-08-1991 CA 2019353 A 09-10-1991 CA 2019353 A 09-10-1991 CA 2019353 A 09-10-1991 DE 69016715 D 23-03-1995 DE 69016715 D 23-03-1995 DE 69016715 T 28-09-1995 DE 69016715 T 28-09-1995 DE 69016716 A 30-01-1991 EP 0410567 A 30-01-1991 EP 04103417 A 20-02-1991 EP 0413417 A 20-02-1991 EP 0413417 A 20-02-1991 EP 0413417 A 20-02-1991 EP 0413417 A 20-02-1991 EP 0410468 A 30-07-1992 FP 041747 B 25-03-1994 FP 041747 B 25-03-1994 NO 178748 B 19-02-1996 NZ 234192 A 20-12-1996 NZ 234192 A 20-12-1996 NZ 234192 A 20-12-1994 PL 165265 B 30-12-1994 PL 165265 B 30-12-1994 PL 165265 B 30-12-1994 PL 165265 A 30-12-1994 US 5726137 A 10-03-1998 CA 2019358 A 21-12-1990 CA 2019358 A 21-12-1990			US AU CN MX WO ZA AT AU CA CN DE DE DE DE P EP FI GR HU JP	50512 49283 10898 93057 94064 93069 1181 1256 6401 57556 20193 10554 690167 690167 690212 04134 04105 04070 04070 04070 9031 901004	50 A 93 A 46 A 90 A 65 T 89 B 43 B 43 B 43 B 43 B 45 T 40 A 416 A 417 A 416 A 417 A 416 A 417 A 416 A 417 A 416 A 417 A 416 A 417 A 418 B 418 B	24 12 27 31 31 20 15 15 19 20 23 23 24 25 26 27 20 27 27 27 27 28 28 28 28 28 28 28 29 20 20 20 20 20 20 20 20 20 20 20 20 20	-09-1991 -04-1994 -07-1994 -05-1994 -03-1995 -02-1995 -08-1995 -08-1995 -08-1991 -10-1991 3-10-1991 3-03-1995 3-09-1995 7-07-1991 3-02-1991 3-02-1991 3-02-1991 3-03-1991 3-03-1991 3-03-1991 3-03-1991 3-03-1991 3-03-1991 3-03-1991 3-03-1991 3-03-1991 3-03-1991 3-03-1991 3-03-1991 3-03-1991 3-03-1991 3-03-1991 3-03-1991 3-03-1991
AT 118165 T 15-02-1995 AT 125689 T 15-08-1995 AU 640143 B 19-08-1993 AU 640143 B 19-08-1993 AU 5755690 A 10-10-1991 CA 2019353 A 09-10-1991 DE 69016715 D 23-03-1995 DE 69016715 T 28-09-1995 DE 69016715 T 28-09-1995 DE 69021288 D 07-09-1995 DE 6902128 D 07-09-1991 EP 0407040 A 09-01-1991 EP 0413417 A 20-02-1991 EP 0413417 A 20-02-1991 EP 047042 A 09-01-1991 GR 9010468 A B 30-07-1992 HU 210756 B 28-07-1995 JP 3291212 A 20-12-1991 MX 173747 B 25-03-1994 NO 178748 B 19-02-1996 NZ 234192 A 26-08-1994 PL 165265 B 30-12-1999 NZ 234192 A 26-08-1994 PL 165265 B 30-12-1999 US 5346736 A 20-09-1994 US 5726137 A 10-03-1998 US 5346642 A 13-09-1994 AT 131034 T 15-12-1995 CA 2019352 A 21-12-1990 CA 2019358 A 21-12-1990 CA 2019358 A 21-12-1990			AT AU AU CA CN DE DE DE DE EP EP FI GR HUD JP	1181 1256 6401 57556 20193 10554 690167 690212 64134 04105 04070 604134 04070 605593 901004	65 T 89 T 43 B 90 A 53 A 82 A 15 D 15 T 88 D 17 T 67 A 1040 A 117 A 117 A 117 A 118 A 118 A 119 A	15 19 10 09 23 23 28 27 28 20 20 20 20 20 20 20 20 20 20 20 20 20	3-02-1995 3-08-1993 3-10-1991 3-10-1991 3-03-1995 3-09-1995 3-09-1995 3-01-1991 3-02-1991 3-02-1991 3-09-1993 3-09-1993 3-07-1995 3-07-1995 3-07-1995
DE 69021288 D 07-09-1995 DK 413417 T 17-07-1995 EP 0410567 A 30-01-1991 EP 0407040 A 09-01-1991 EP 0413417 A 20-02-1991 EP 0413417 A 20-02-1991 EP 0407042 A 09-01-1991 EP 0559304 A 08-09-1993 FI 903130 A 08-09-1993 FI 903130 A 30-07-1992 GR 90100468 A,B 30-07-1992 HU 210756 B 28-07-1995 JP 3291212 A 20-12-1991 MX 173747 B 25-03-1994 NO 178748 B 19-02-1996 NZ 234192 A 26-08-1994 PL 165265 B 30-12-1994 PL 165265 B 30-12-1994 PT 94423 A,B 31-10-1991 US 5348736 A 20-09-1994 US 5726137 A 10-03-1998 US 5346642 A 13-09-1994 AT 131034 T 15-12-1995 AU 5755890 A 03-01-1991 CA 2019352 A 21-12-1990 CA 2019358 A 21-12-1990			DE DK-1 EP EP EP FI GR HU	690212 04105 04105 04070 04134 04070 05593 901004	888 D 17 T 67 A 140 A 117 A 142 A 304 A 30 A 168 A, B	07 17 30 30 40 40 40 40 40 40 40 40 40 40 40 40 40	7-09-1995 7-07-1995 0-01-1991 0-01-1991 0-02-1991 0-02-1991 0-01-1991 0-01-1991 0-07-1992 8-07-1995
FI 903130 A 10-10-1991 GR 90100468 A,B 30-07-1992 HU 210756 B 28-07-1995 JP 3291212 A 20-12-1991 MX 173747 B 25-03-1994 NO 178748 B 19-02-1996 NZ 234192 A 26-08-1994 PL 165265 B 30-12-1994 PT 94423 A,B 31-10-1991 US 5348736 A 20-09-1994 US 5726137 A 10-03-1998 US 5346642 A 13-09-1994 AT 131034 T 15-12-1995 AU 5755890 A 03-01-1991 CA 2019352 A 21-12-1990 CA 2019358 A 21-12-1990		1 (7.3	FI GR HU JP	9031 901004 2107	.30 A 168 A,B 756 B	ੂੰ ਕੂੰ ਹੈ। 30	0-10-1991 0-07-1992 3-07-1995
PT 94423 A,B 31-10-1991 US 5348736 A 20-09-1994 US 5726137 A 10-03-1998 US 5346642 A 13-09-1994 AT 131034 T 15-12-1995 AU 5755890 A 03-01-1991 CA 2019341 A 21-12-1990 CA 2019352 A 21-12-1990 CA 2019358 A 21-12-1990			NO NZ	1737 1787 2341	747 B 748 B 192 A	20 25 19 26 26	5-03-1994 9-02-1996 5-08-1994
な さん 数3 (2 M (NB) は 1 M (NB) は	·	v 13 - (97	PT US US US AT AU CA	944 53487 57261 53466 1310 57558 20193 20193	123 A,B 736 A 137 A 542 A 034 T 390 A 341 A 352 A	33 20 10 11 11 03 22 22	1-10-1991 0-09-1994 0-03-1998 3-09-1994 5-12-1995 3-01-1991 1-12-1990
	: : :	ng ng C ng s <b>a</b> kk			de la servición de la servició		
	**	guri e u u u u u u u u u u u u u u u u u u					,

Information on patent family members

PCT/IB 98/00651

	atent document d in search report		Publication date		Patent family member(s)	Publication date
US	5580494	Α		CN	1048422 A	09-01-1991
•				DE	69023969 D	18-01-1996
		:		EP	0407041 A	09-01-1991
				GR	90100471 A	15-11-1991
	•			JP	3051367 A	05-03-1991
				.PT	94418 A	08-02-1991
				US.	5415857 A	16-05-1995
				AU	628590 B	17-09-1992
WO	9406403	Α	31-03-1994	AU	674340 B	19-12-1996
				AU	4928593 A	12-04-1994
				CN	1087513 A	08-06-1994
				EP	0661962 A	12-07-1995
				MX	9305744 A	31-05-1994
				ZA	9306926 A	20-03-1995
WO	9729736	Α	21-08-1997	AU	1720897 A	02-09-1997
WO	9725975	Α	24-07-1997	AU	1699597 A	11-08-1997
WO	9726860	Α	31-07-1997	AU	1709997 A	20-08-1997
US	5391368	Α	21-02-1995	ES	2100121 A	01-06-1997
				GB	2281913 A,B	22-03-1995
WO	9210162	Α	25-06-1992	AT	111727 T	15-10-1994
				AU	666642 B	22-02-1996
				AU	9117791 A	08-07-1992
				CA	2097836 A,C	06-06-1992
				CN	1062837 A,B	22-07-1992
				DE	69104224 D	27-10-1994
				DE	69104224 T	09-03-1995
				DK	560919 T	06-03-1995
				EG	19564 A	29-06-1995
				EP	0560919 A	22-09-1993
				ES	2060467 T	16-11-1994
	•			, FI	932565 A	04-06-1993
				HU	64686 A	28-02-1994
				IE	64892 B	20-09-1995
				JP	6503574 T	21-04-1994

I. national Application No

Inform	ation on patent family me	nbers	į	98/00651
Patent document cited in search report	· Publication date	Patent fa membe	mily r(s)	Publication date
WO 9210162 A		NZ 24 PL 16 PT SK	02411 A 40856 A 57653 B 99687 A 56893 A 73709 A	31-01-1994 24-02-1995 31-10-1995 30-10-1992 11-05-1994 12-11-1996
WO 9818433 A	07-05-1998	AU 46	45097 A	22-05-1998
1000 1000				: :
en e	A. A			
1		en tora. Postoral		
1.03 8.799.00 Q	188 - 176 - 77 - 286			•
		and the second of the second		
		grander of the second		

THIS PAGE BLANK (USPTO)